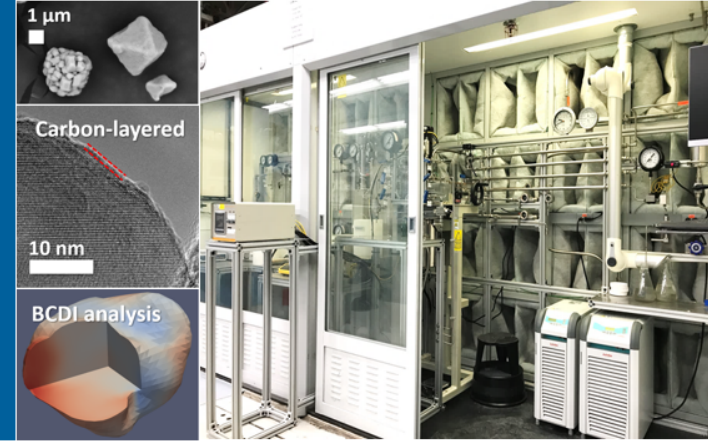


Process R&D Using Supercritical Fluid Reactors



Youngho Shin (PI)

Seokhun Kim

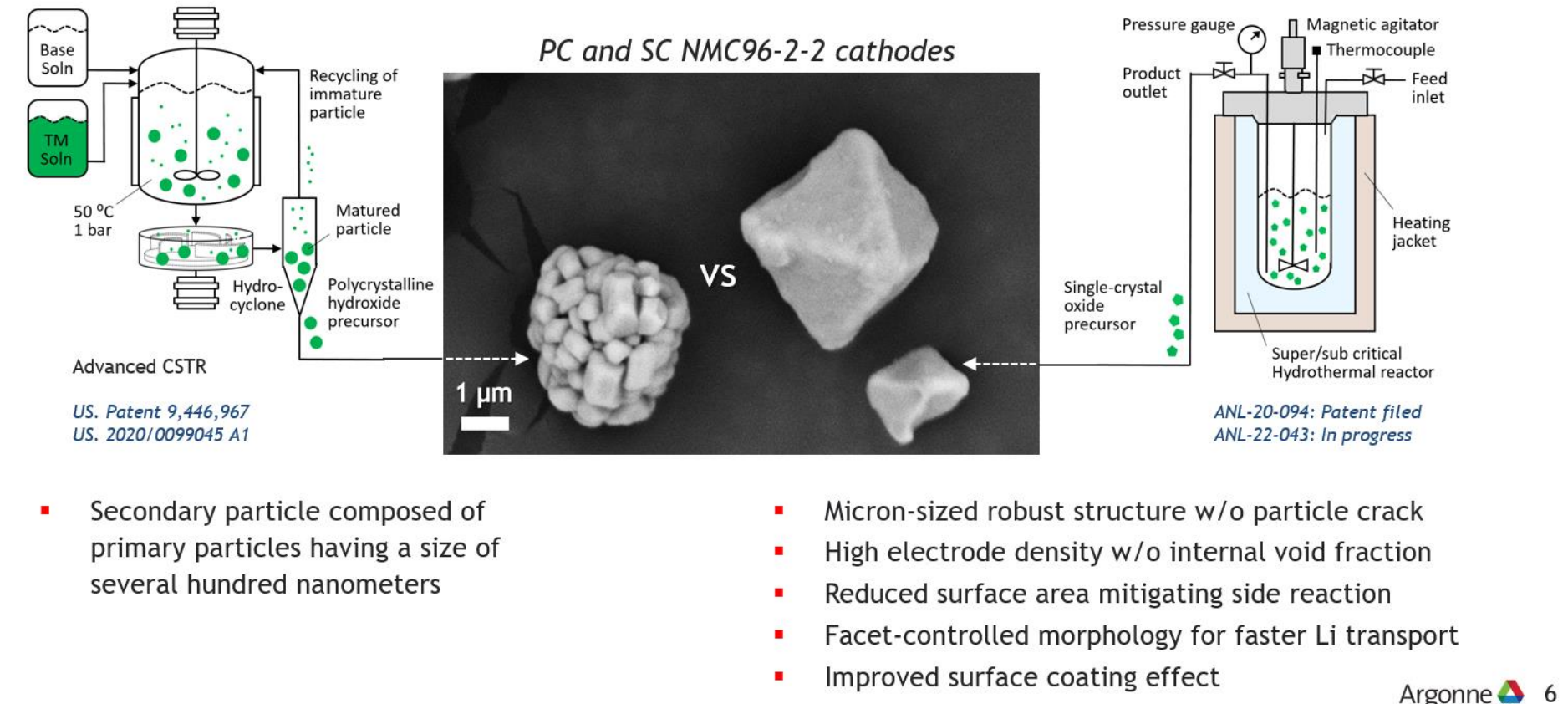
Argonne National Laboratory
Project ID: BAT470

June 2022

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Approach : Polycrystalline & Single-crystal NMC96-2-2

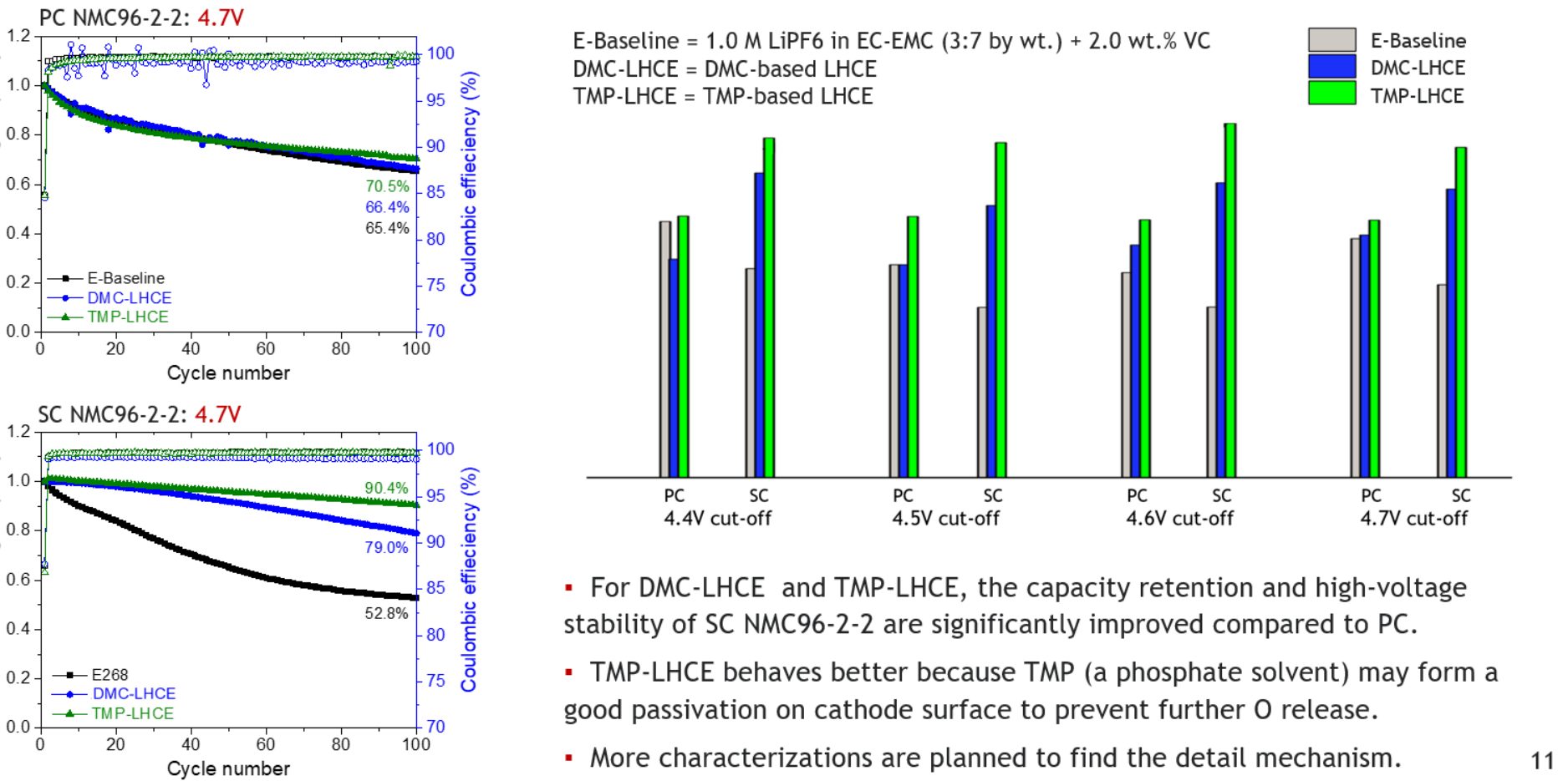
- Polycrystalline cathode particle
- Single-crystal cathode particle



- Secondary particle composed of primary particles having a size of several hundred nanometers
- Micron-sized robust structure w/o particle crack
- High electrode density w/o internal void fraction
- Reduced surface area mitigating side reaction
- Facet-controlled morphology for faster Li transport
- Improved surface coating effect

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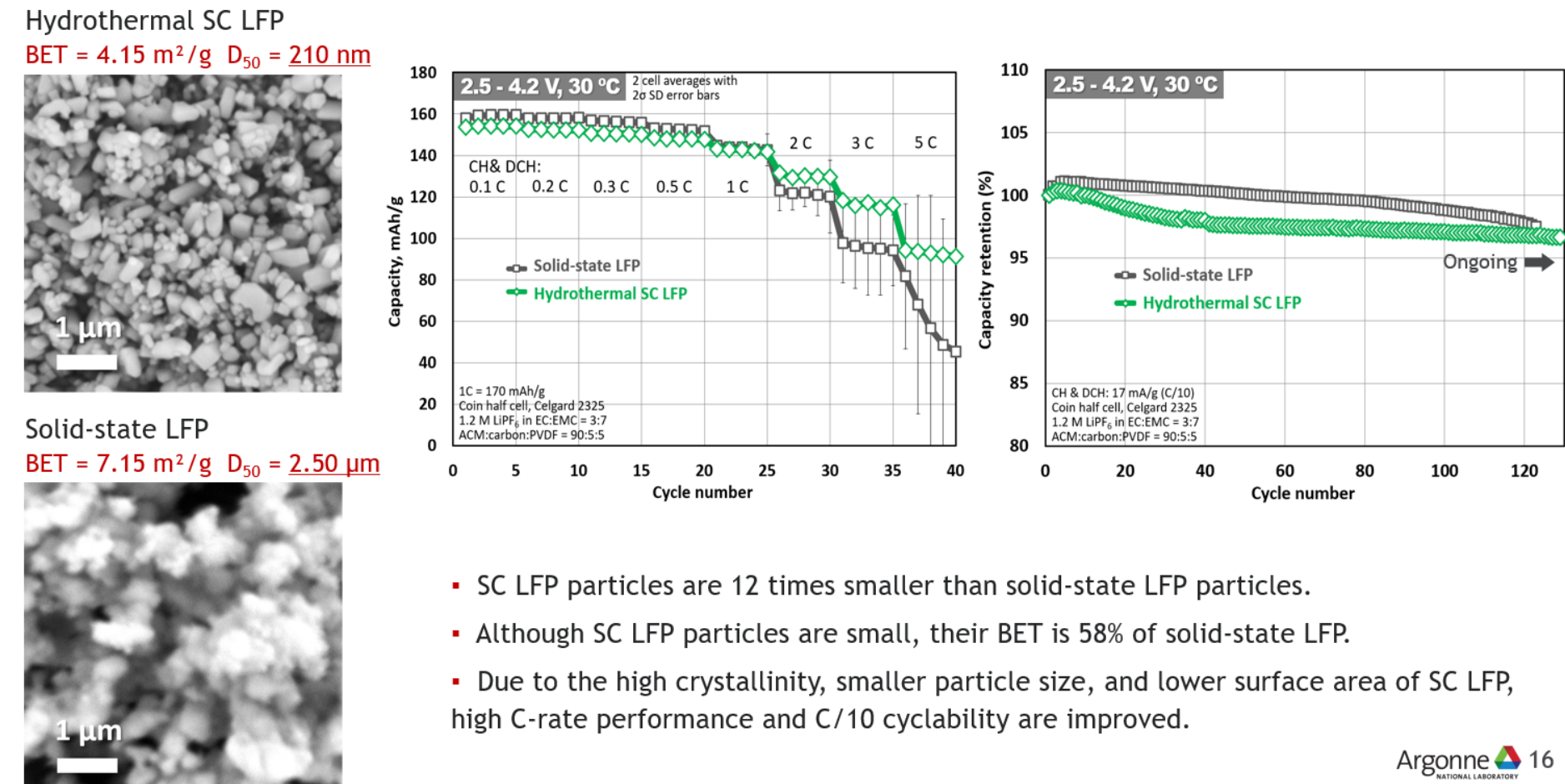
Technical Accomplishments and Progress Improved Cyclability by Selected Electrolyte: 2



- For DMC-LHCE and TMP-LHCE, the capacity retention and high-voltage stability of SC NMC96-2-2 are significantly improved compared to PC.
- DMC-LHCE behaves better than TMP (a phosphate solvent) may form a good passivation on cathode surface to prevent further O release.
- More characterizations are planned to find the detail mechanism.

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Technical Accomplishments and Progress Performance of SC LFP Compared to Solid-state LFP



- SC LFP particles are 12 times smaller than solid-state LFP particles.
- Although SC LFP particles are small, their BET is 58% of solid-state LFP.
- Due to the high crystallinity, smaller particle size, and lower surface area of SC LFP, high C-rate performance and C/10 cyclability are improved.

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Responses to Previous Year Reviewers' Comments

- "This reviewer commented that the single crystal NMC particles have no grain boundaries and are more robust than polycrystalline cathode particles. The density of single crystal particles is also higher than polycrystalline powders. The reviewer indicated that this is a nice approach to making a better performing cathode."
- "If this project does produce materials that are of interest for commercialization or scale-up beyond 40 grams, it is unclear whether this process is truly scalable to a kg scale or what the alternate process approach would be to help scale-up synthesis of the most promising materials. Is there an exit strategy for this project when a promising material is found?"
 - Response:** A transition is taking place from the existing batch hydrothermal process to a continuous-flow rapid hydrothermal process (200-gm CAM/hr) for material scale-up. This project serves as a cornerstone and leads to technology transfer to an industry partner who plans to commercialize the continuous-flow hydrothermal process.
- "The reviewer further noticed the electrode composition is quite high in binder and carbon content (70:15:15) and inquired about the reason for that. How do these materials perform at higher charge and discharge rates?"
 - Response:** When making the cathode electrode, the binder and carbon content were kept high to connect the single-crystal particles (which are significantly smaller than the polycrystalline particles). Now, the cathode electrode making process has been improved and 90:5:5 ratio is applied and the electrochemical test results using this electrode shows significantly improved performance at higher charge and discharge rates.

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Overview

Timeline

- Project start date: Oct. 2019
- Project end date: Sept. 2022
- Percent complete: On-going

Budget

- Total project funding:
 - \$ 600K in FY22

Barriers

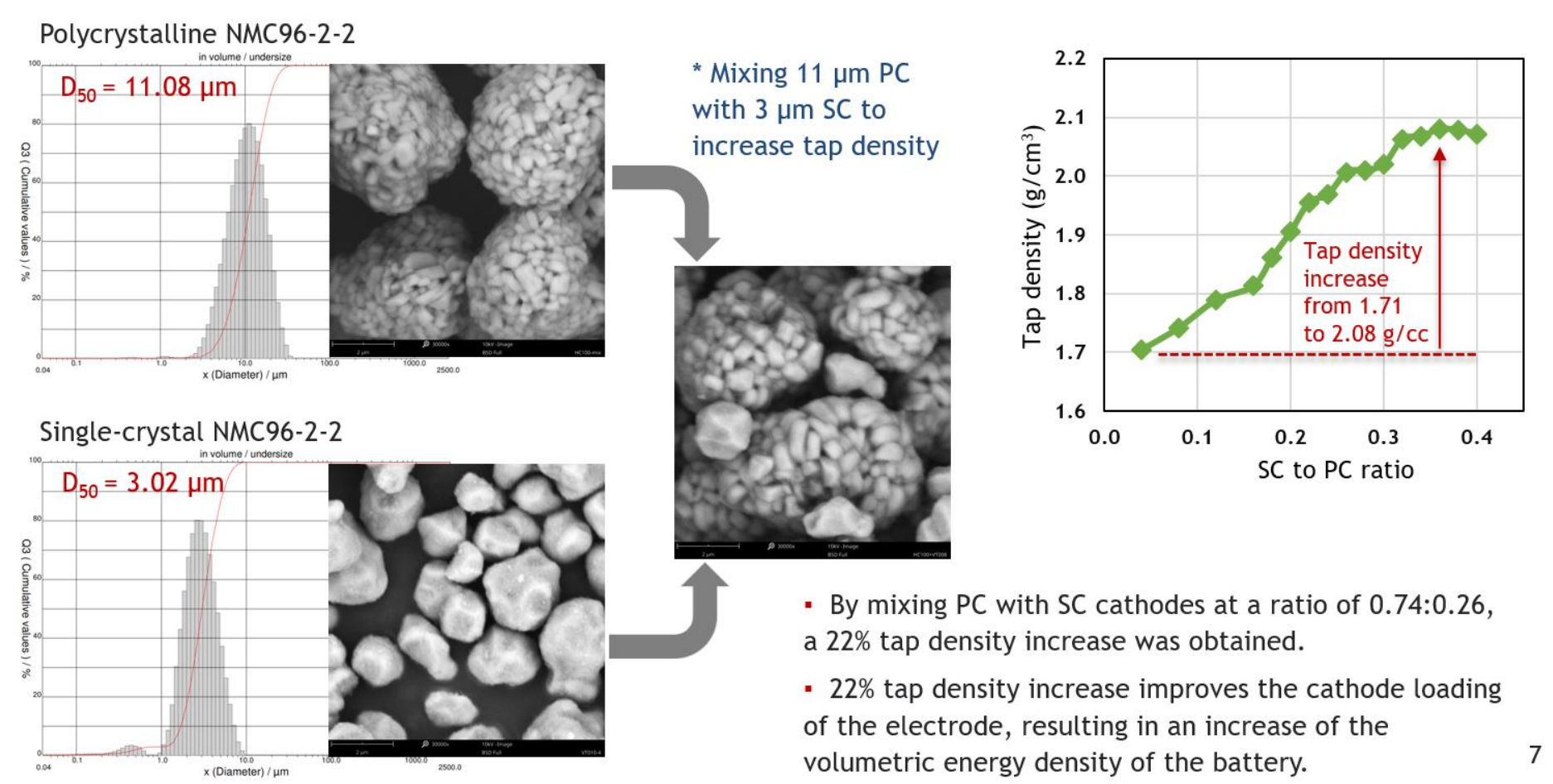
- Advanced synthesis processes and materials are needed to improve battery performance.
- New active battery materials with desired particle size, morphology, and composition distribution are not commercially available.

Partners

- Battery material process R&D:
 - University of Wisconsin
 - University of California, Irvine
 - HRTEM
 - Pacific Northwest National Laboratory
 - Electrolyte for single-crystal cathode
 - Northwestern University
 - TEM analysis for carbon-coating
 - Argonne Post-Test Facility
 - XPS surface analysis
 - Hunt Energy / Argonne AMD
 - ALD oxide surface coating
 - Argonne APS
 - Bragg coherent X-ray diffraction imaging

Argonne 2

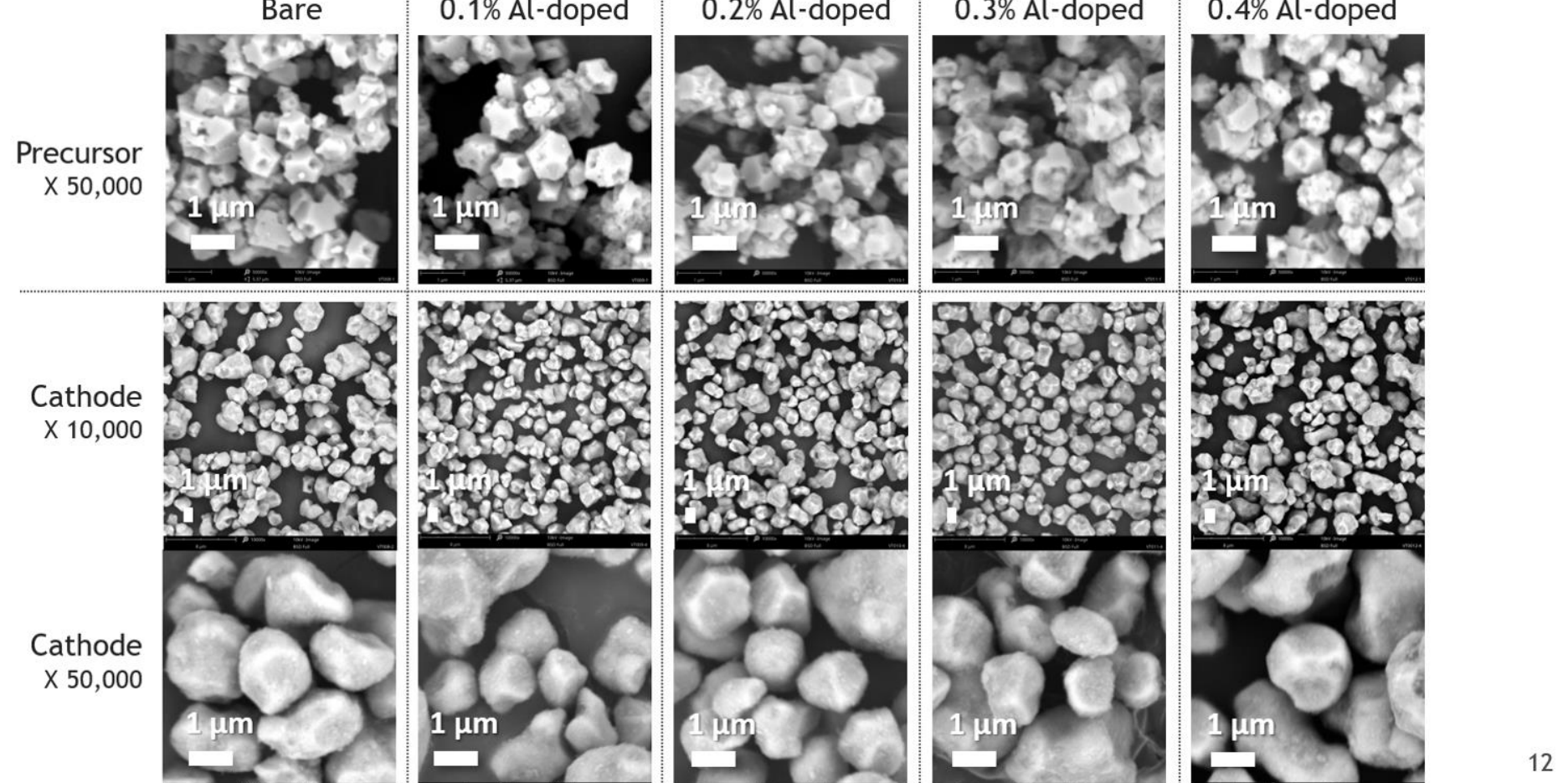
Technical Accomplishments and Progress Tap Density Increase by Mixing PC & SC NMC96-2-2



- By mixing PC with SC cathodes at a ratio of 0.74:0.26, a 22% tap density increase was obtained.
- 22% tap density increase improves the cathode loading of the electrode, resulting in an increase of the volumetric energy density of the battery.

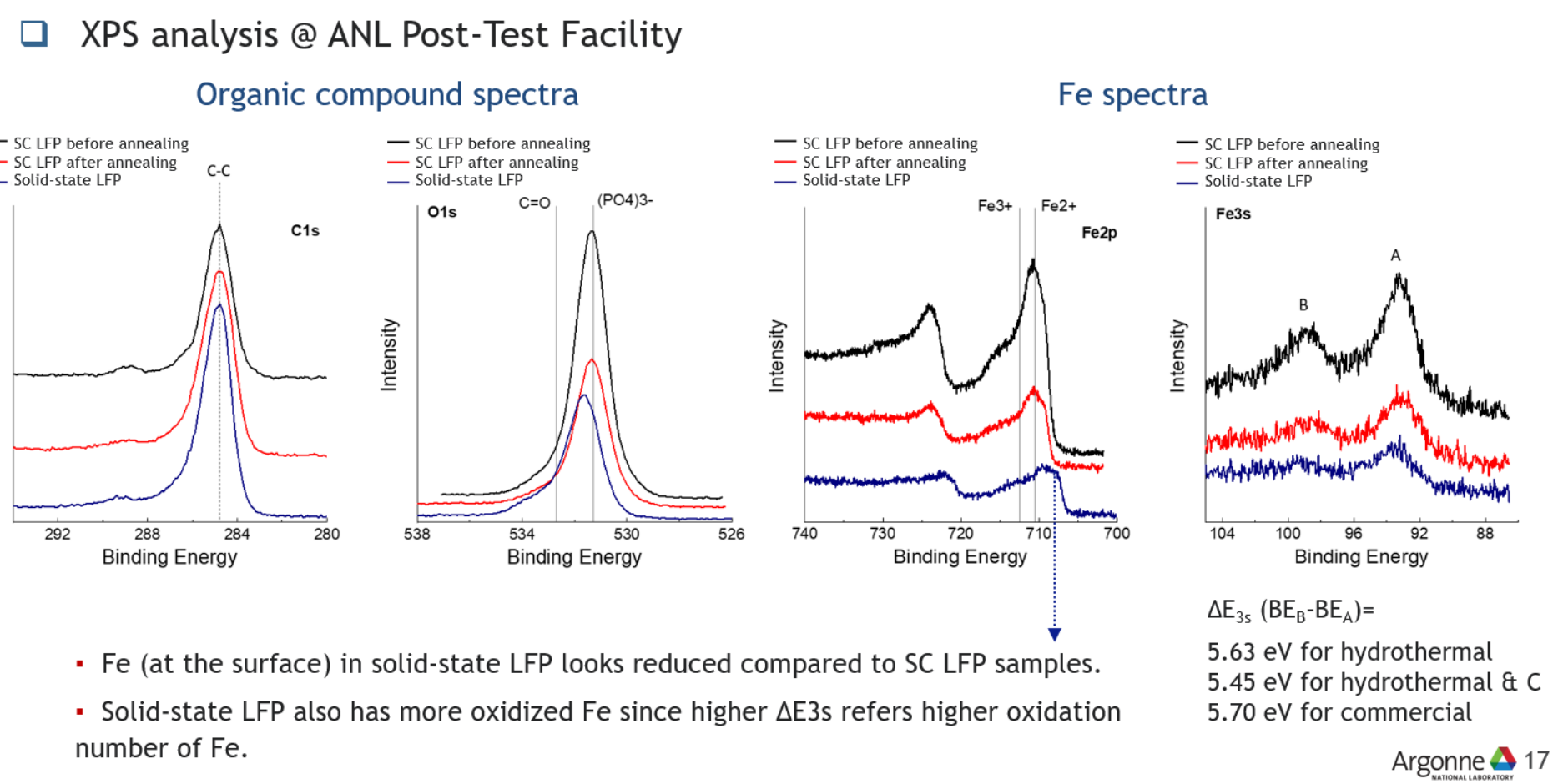
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Technical Accomplishments and Progress Synthesis of Al-doped SC NMC96-2-2



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Technical Accomplishments and Progress Reduced Impurities of Hydrothermal SC LFP



- Fe (at the surface) in solid-state LFP looks reduced compared to SC LFP samples.
- Solid-state LFP also has more oxidized Fe since higher ΔE_{3s} refers higher oxidation number of Fe.

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Collaboration and Coordination

- University of Wisconsin:** Nano-indentation of polycrystalline and single-crystal NMC96-2-2 cathode
- University of California, Irvine:** HRTEM and FIB cross-sectional elemental mapping of single-crystal NMC96-2-2 cathode
- Pacific Northwest National Laboratory:** Electrolyte study to enhance the capacity retention of Ni-rich NMC96-2-2
- Northwestern University:** TEM analysis for carbon-layered single-crystal LFP
- Argonne Post-Test Facility:** XPS analysis of pristine and ALD-coated polycrystalline and single-crystal NMC96-2-2 and LFP cathodes
- Hunt Energy:** Industrial evaluation and ALD Ti/Al double oxide coating of single-crystal NMC96-2-2
- Argonne APS:** BCDI analysis on single-crystal LFP

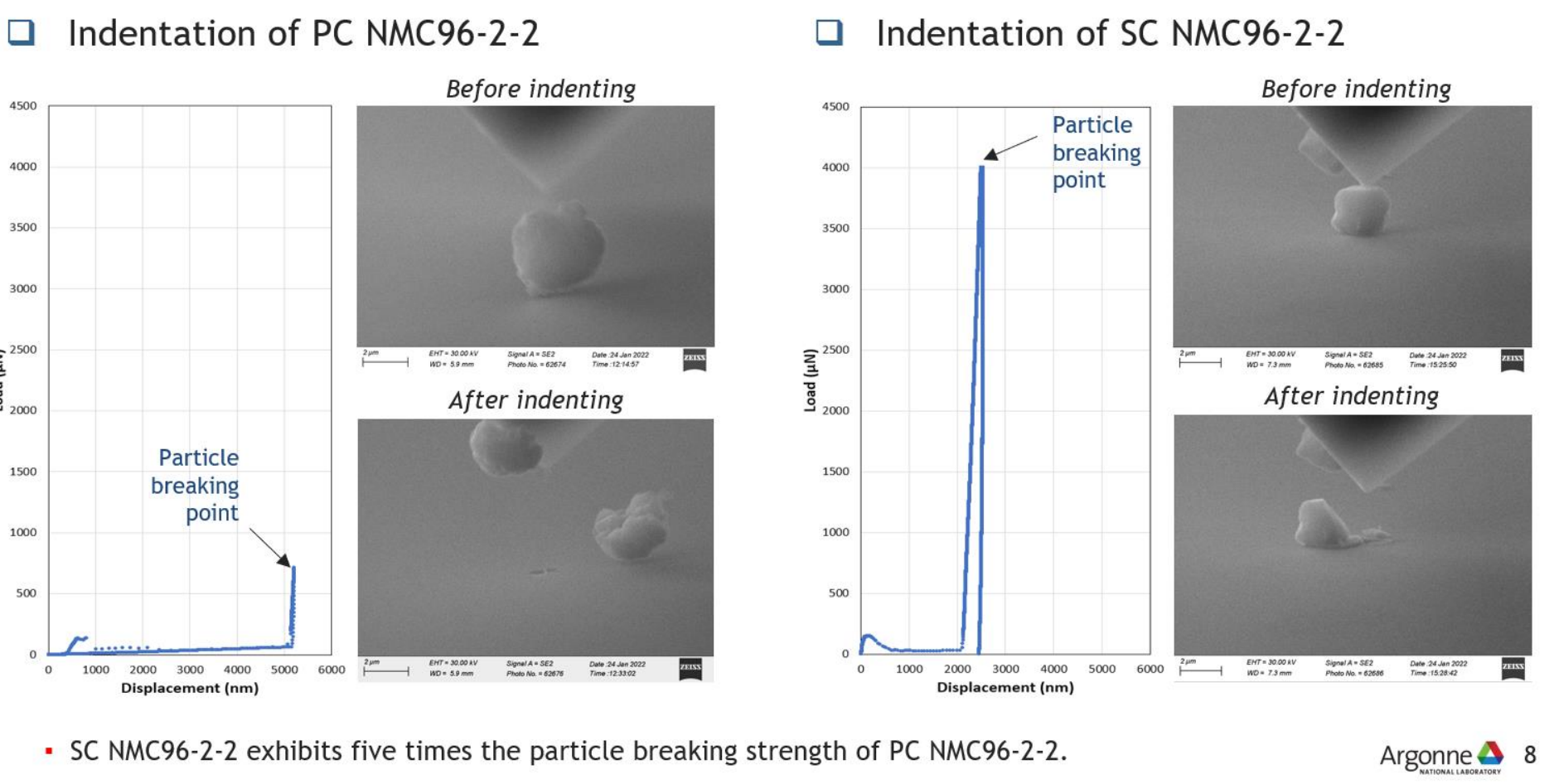
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Relevance

- The relevance of this program to the DOE Vehicle Technologies Program is:
 - Emerging synthesis processes need to be explored to enable rapid robust reproducible manufacturing of active battery materials.
 - This program is a key missing link between the discovery of advanced battery materials, market evaluation of these materials, and high-volume manufacturing.
 - It reduces the risk associated with the synthesis process development and scale-up of new battery materials.
- The objective of this program is to establish flexible R&D capability of supercritical fluid reactions as an emerging manufacturing process for active battery materials:
 - Develop a robust and reproducible hydro-solvent (HYST) synthesis process to assure economic feasibility and scale-up strategies.
 - Produce and provide single-crystal battery materials with desired particle size, morphology, and composition distribution to support fundamental research.
 - Characterize single-crystal battery materials and improve their high-rate capability and long-term cyclability by synthesis process optimization.

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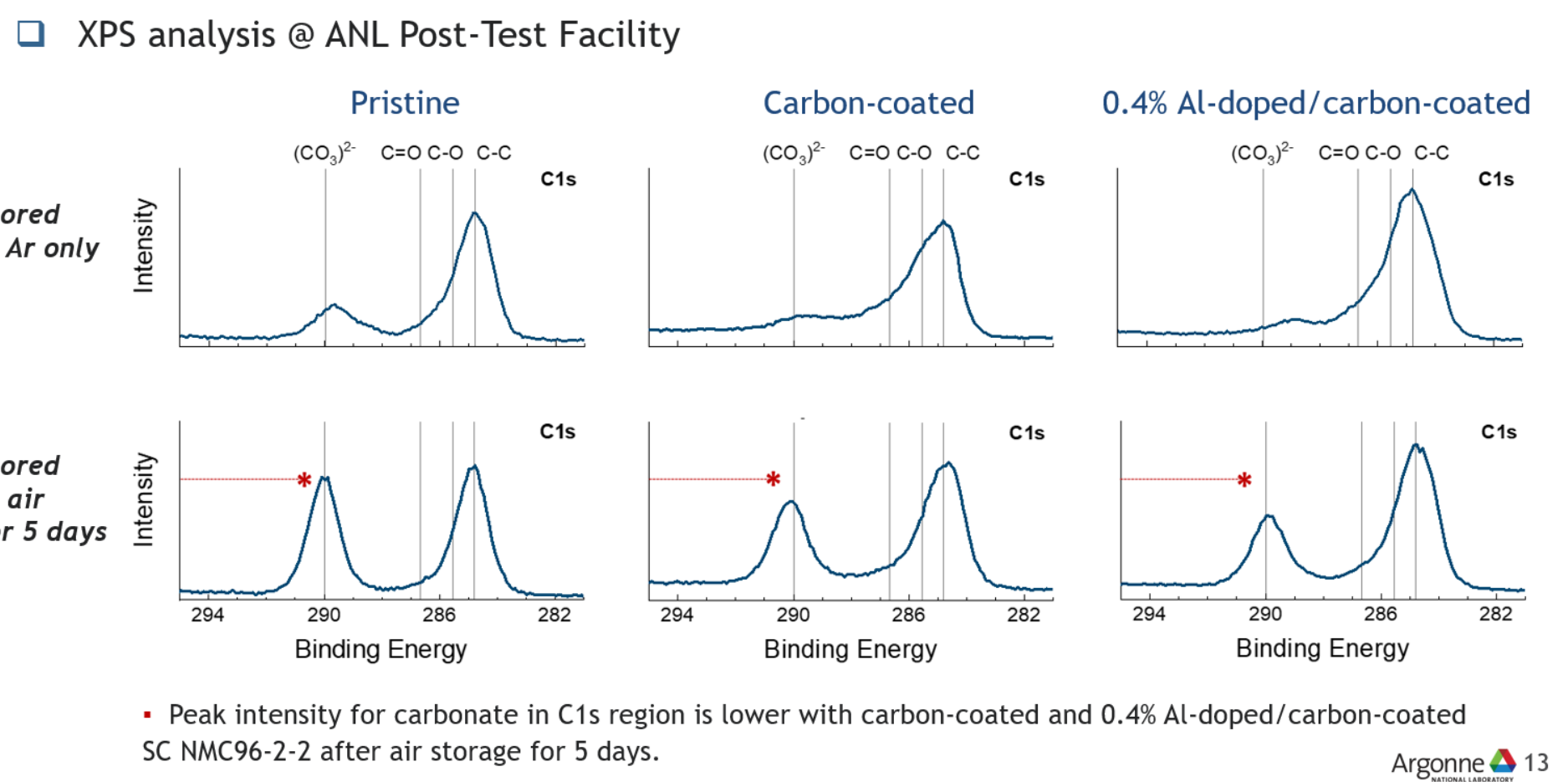
Technical Accomplishments and Progress Particle Crack Analysis by Nano-indentation



- SC NMC96-2-2 exhibits five times the particle breaking strength of PC NMC96-2-2.

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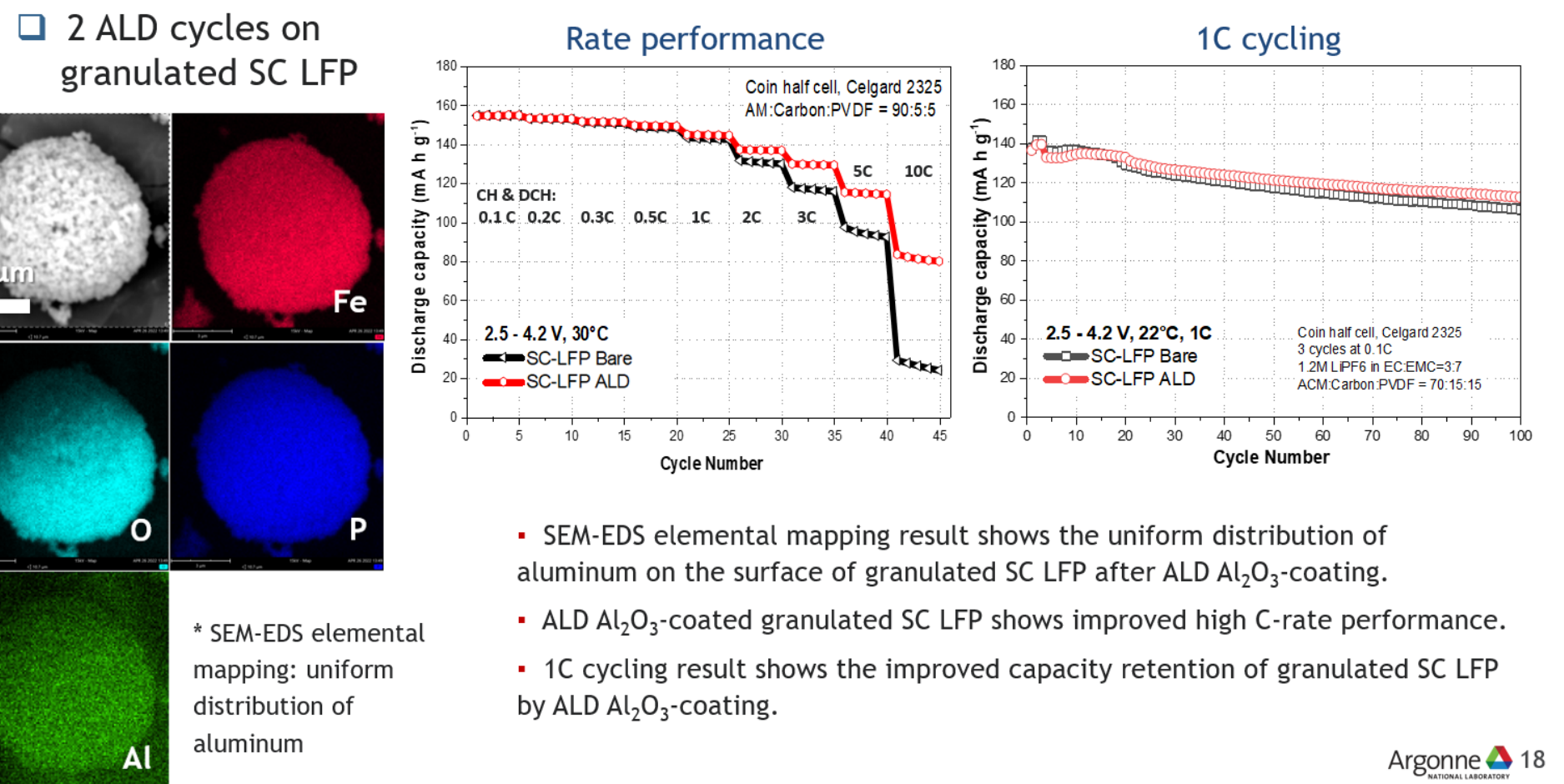
Technical Accomplishments and Progress Surface Protection of SC NMC96-2-2



- Peak intensity for carbonate in C1s region is lower with carbon-coated and 0.4% Al-doped/carbon-coated SC NMC96-2-2 after air storage for 5 days.

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Technical Accomplishments and Progress ALD Al₂O₃-coated Granulated SC LFP



- SEM-EDS elemental mapping result shows the uniform distribution of aluminum on the surface of granulated SC LFP after ALD Al₂O₃-coating.
- ALD Al₂O₃-coated granulated SC LFP shows improved high C-rate performance.
- 1C cycling result shows the improved capacity retention of granulated SC LFP by ALD Al₂O₃-coating.

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Proposed Future Research (FY22-23)

- Operation of continuous-flow rapid hydrothermal process
 - Hydrothermal synthesis technology transfer from batch to continuous process
 - Develop a process for single-crystal particle granulation
 - Develop a process for carbon single-crystal particle composite
- Produce Kg-level carbon-layered grain-free single-crystal LFP/LFMP
- Produce Kg-level granulated carbon LFP/LFMP composite
- Produce Kg-level grain-free single-crystal low-cobalt NMC
- Produce Kg-level granulated carbon low-cobalt NMC composite

Any proposed future work is subject to change based on funding levels

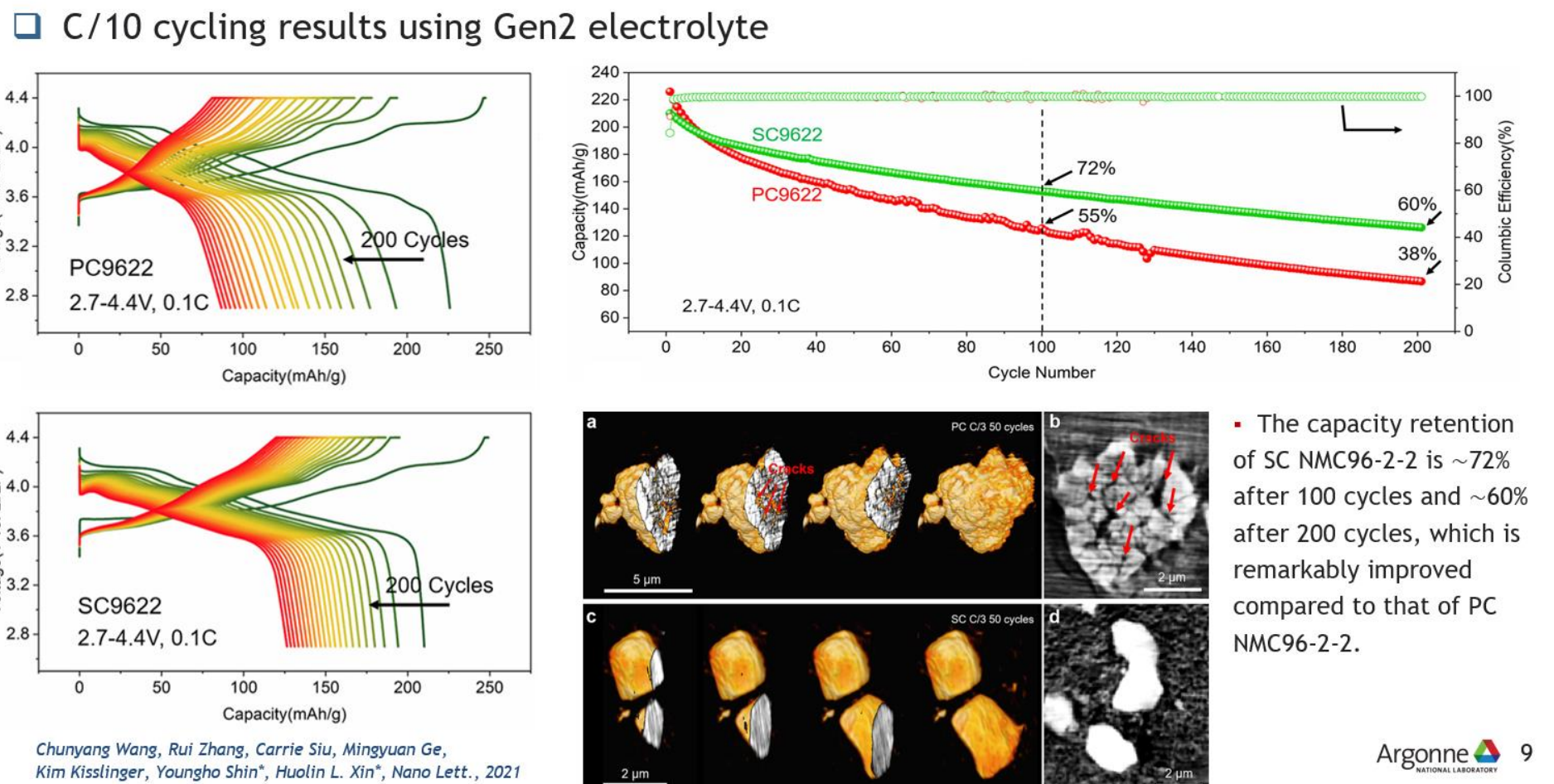
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Approach : Milestones

2021	Synthesis process optimization of single-crystal NMC96-2-2 cathode <ul style="list-style-type: none"> Synthesis process optimization for improved particle size, distribution, and morphology Tap density increase by mixing polycrystalline & single-crystal NMC96-2-2 Particle strength measurement of polycrystalline & single-crystal NMC96-2-2 (collaboration) 	Completed	Q4
	Performance improvement of single-crystal NMC96-2-2 cathode <ul style="list-style-type: none"> Electrolyte impact assessment on single-crystal NMC96-2-2 (collaboration) Carbon coating on single-crystal NMC96-2-2 ALD TiO₂-Al₂O₃ double oxide coating on single-crystal NMC96-2-2 (collaboration) 	Completed	Q1
	Synthesis of nano-sized carbon-layered single-crystal LFP cathode <ul style="list-style-type: none"> Hydrothermal production of carbon-layered single-crystal LFP to enable fast charge Characterization of the prepared carbon-layered single-crystal LFP ALD Al₂O₃ oxide coating on single-crystal LFP (collaboration) 	Completed	Q1
2022	Synthesis of Al-doped single-crystal NMC96-2-2 cathodes <ul style="list-style-type: none"> Production of 0.1 - 0.4% Al-doped single-crystal NMC96-2-2 cathodes Carbon coating on Al-doped single-crystal NMC96-2-2 ALD TiO₂-Al₂O₃ double oxide coating on Al-doped single-crystal NMC96-2-2 (collaboration) 	In-progress	Q2
	Operation of continuous-flow rapid hydrothermal process <ul style="list-style-type: none"> Produce Kg-level carbon-layered grain-free single-crystal LFP/LFMP Produce Kg-level grain-free single-crystal low-cobalt NMC 	go/no-go	Q3

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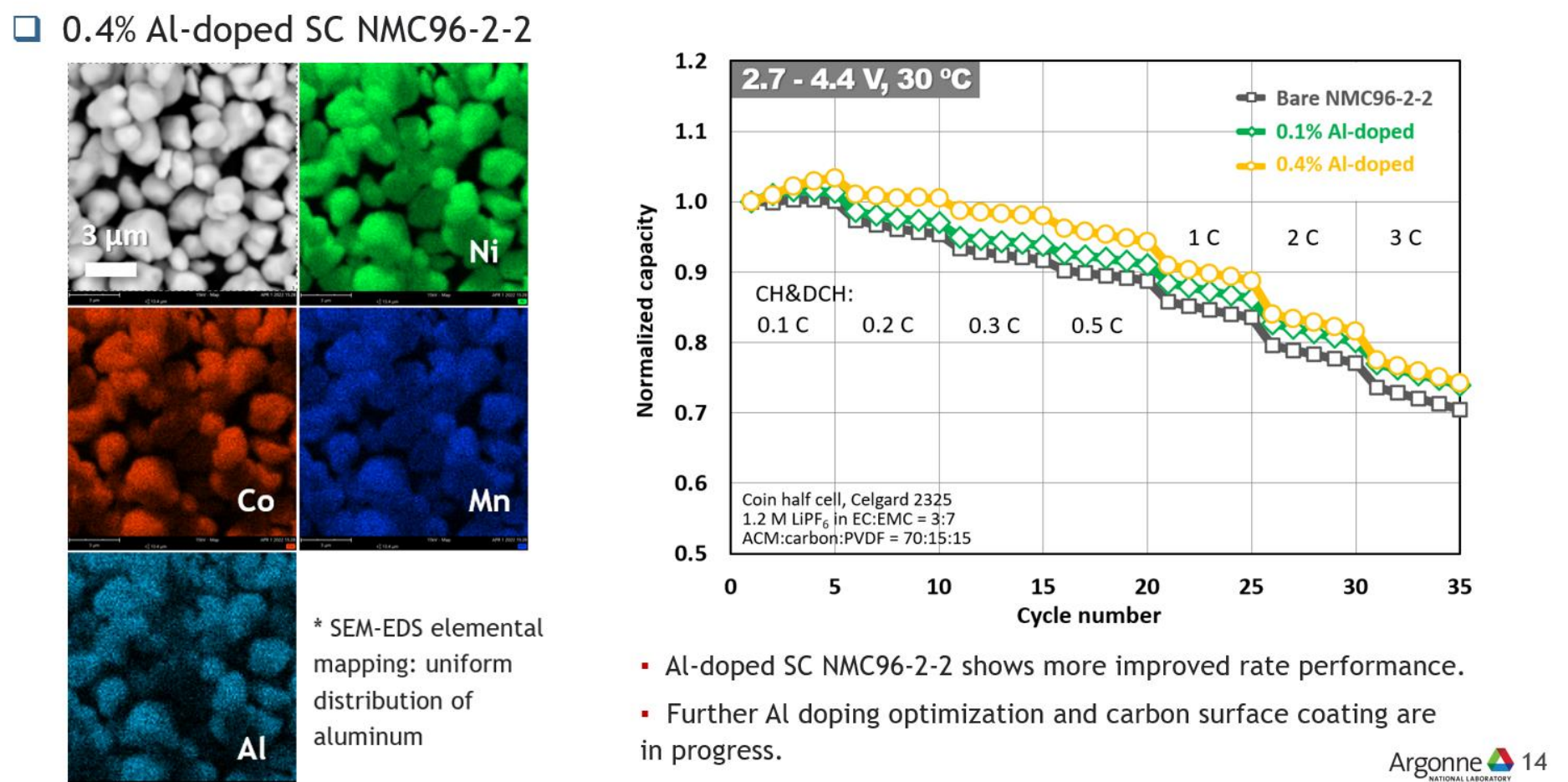
Technical Accomplishments and Progress Cycling Performance of PC & SC NMC96-2-2



- The capacity retention of SC NMC96-2-2 is ~72% after 100 cycles and ~60% after 200 cycles, which is remarkably improved compared to that of PC NMC96-2-2.

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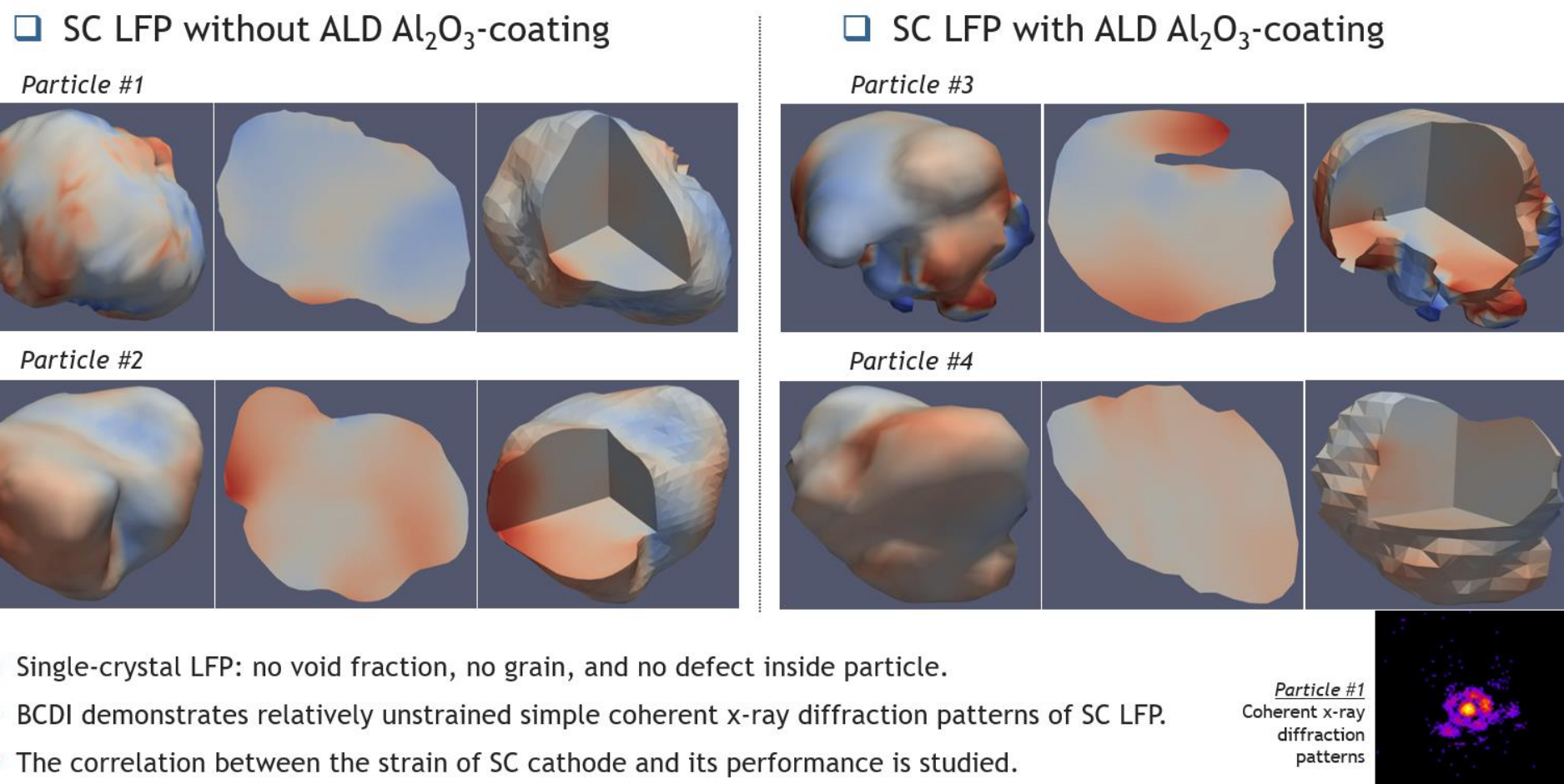
Technical Accomplishments and Progress Optimization of Al-doped SC NMC96-2-2



- Al-doped SC NMC96-2-2 shows more improved rate performance.
- Further Al doping optimization and carbon surface coating are in progress.

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Technical Accomplishments and Progress BCDI analysis on SC LFP



- Single-crystal LFP: no void fraction, no grain, and no defect inside particle.
- BCDI demonstrates relatively unstrained simple coherent x-ray diffraction patterns of SC LFP.
- The correlation between the strain of SC cathode and its performance is studied.

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Summary

- By mixing PC with SC cathodes at a ratio of 0.74:0.26, a 22% tap density increase was obtained, which improves the cathode electrode loading and the volumetric energy density of the battery.
- SC NMC96-2-2 exhibits five times the particle breaking strength of PC NMC96-2-2.
- The capacity retention of SC NMC96-2-2 is ~72% after 100 cycles and ~60% after 200 cycles, which is remarkably improved compared to that of PC NMC96-2-2.
- For DMC-LHCE and TMP-LHCE electrolytes, the capacity retention and high-voltage stability of SC are better than PC at the same condition.
- Peak intensity for carbonate in C1s region is lower with carbon-coated and 0.4% Al-doped/carbon-coated SC NMC96-2-2 after air storage for 5 days.
- Al-doped SC NMC96-2-2 shows more improved rate performance.
- SC LFP particles are 12 times smaller than solid-state LFP particles. Due to the less impurities, high crystallinity, smaller particle size, and lower surface area of SC LFP, high C-rate performance and C/10 cyclability are improved.
- ALD Al₂O₃-coated SC LFP shows improved high C-rate performance and 1C cycling capacity retention.
- BCDI analysis demonstrates no grain, no dislocation, no defect, and no void fraction inside particle, and relatively unstrained simple coherent x-ray diffraction patterns of SC LFP.

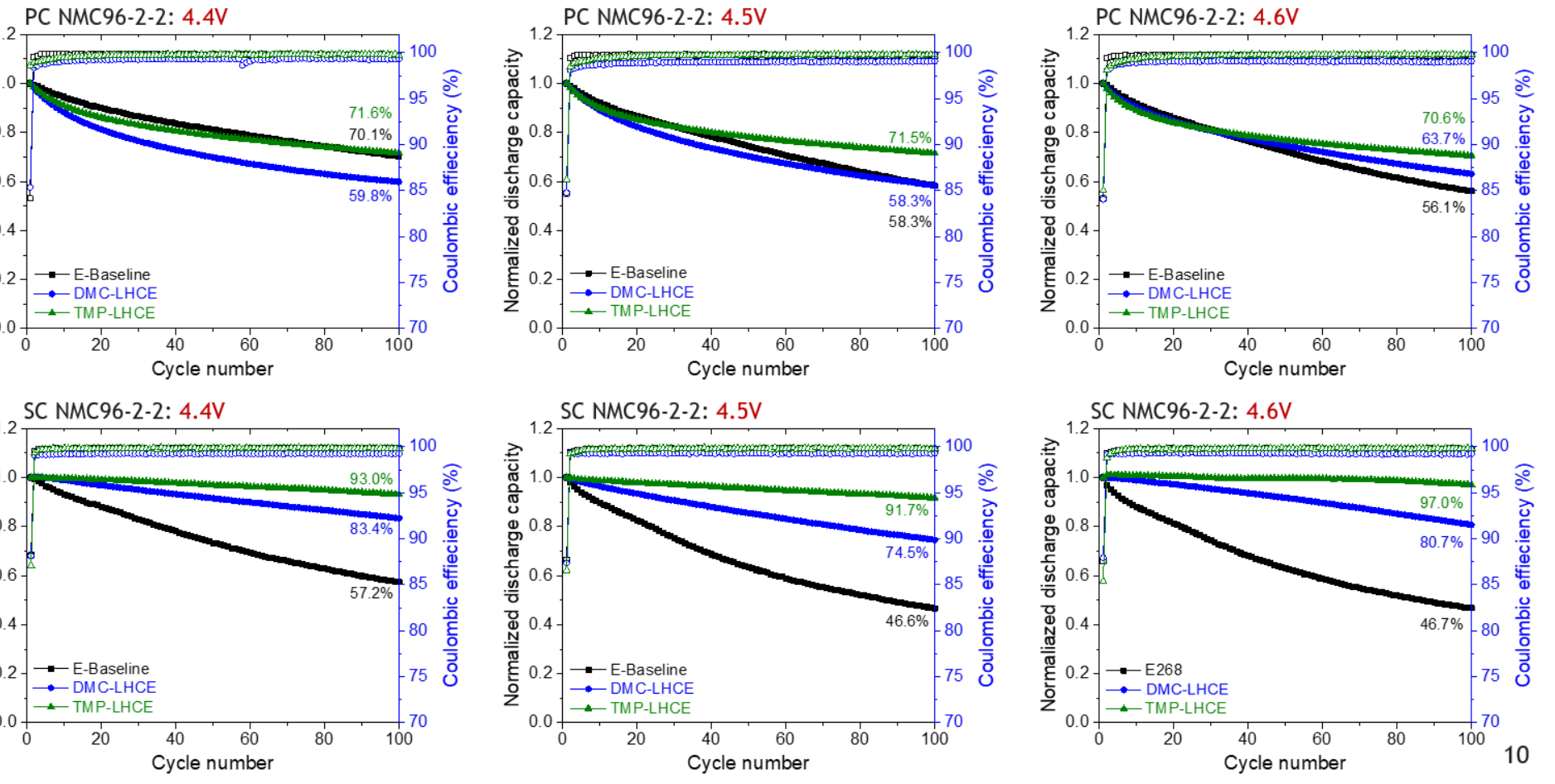
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Approach : Strategy

- Hydro-solothermal process, expandable to mass production, is one of the most important synthesis routes to produce single-crystal particle.
- Hydro-solothermal process can tailor the morphology of single-crystal particle by changing the reactant, concentration, pressure, temperature, and mineralizer.
- Establish a flexible hydro-solothermal synthesis platform to produce advanced single-crystal battery materials with desired particle size, morphology, and composition distribution.
- Provide single-crystal battery materials with advanced features to support basic researchers and to facilitate industrial evaluation:
 - 1-3 micron single-crystal particle without internal void fraction to enhance electrode density
 - Robust particle structure to suppress particle crack during cycling
 - Reduced surface area to mitigate side reaction with electrolyte
 - Facet-controlled particle morphology to enable faster lithium transport

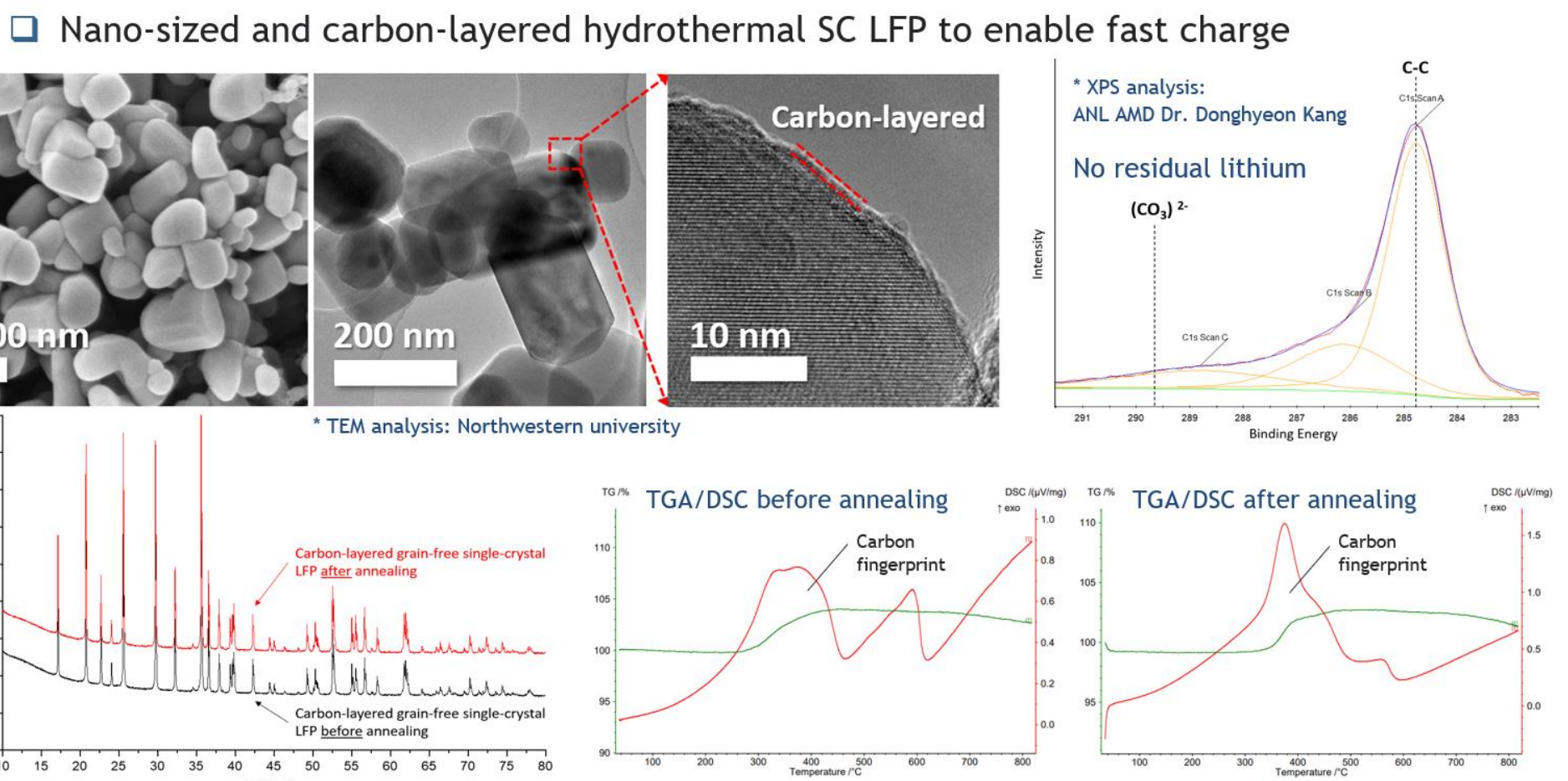
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Technical Accomplishments and Progress Improved Cyclability by Selected Electrolyte: 1



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Technical Accomplishments and Progress Synthesis of Nano-sized Carbon-layered SC LFP



- For DMC-LHCE and TMP-LHCE, the capacity retention and high-voltage stability of SC NMC96-2-2 are significantly improved compared to PC.
- DMC-LHCE behaves better than TMP (a phosphate solvent) may form a good passivation on cathode surface to prevent further O release.
- More characterizations are planned to find the detail mechanism.

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Technical Accomplishments and Progress Material Delivery to Support Research Groups

Material delivered	Date	Collaborator	Material delivered	Date	Collaborator
SC NMC9622 precursor	Sep. 2021	University of California Irvine	SC NMC9622 cathode	Feb. 2022	NERL
SC NMC9622 cathode	Sep. 2021	University of California Irvine	SC NMC9622 cathode	Mar. 2022	ANL CSE
SC NMC9622 laminate	Sep. 2021	University of California Irvine	SC NMC9622 + 0.25 Al cathode	Mar. 2022	ANL CSE
Gradient PC NMC9622	Oct. 2021	University of California Irvine	SC NMC9622 + 0.15 Al cathode	Mar. 2022	ANL Post-Test Facility
Gradient PC NMC9622	Oct. 2021	University of California Irvine	SC NMC9622 + 0.25 Al cathode	Mar. 2022	ANL Post-Test Facility
PC NMC9622 cathode	Nov. 2021	PNINL	SC NMC9622 + 0.35 Al cathode	Mar. 2022	ANL Post-Test Facility
PC NMC9622 cathode	Nov. 2021	PNINL	SC NMC9622 + 0.45 Al cathode	Mar. 2022	ANL Post-Test Facility
SC NMC9622 cathode	Nov. 2021	PNINL	SC NMC9622 + 0.55 Al cathode	Mar. 2022	ANL Post-Test Facility
SC NMC9622 cathode	Nov. 2021	PNINL	SC NMC9622 + 0.65 Al cathode	Mar. 2022	ANL Post-Test Facility
SC LFP cathode	Dec. 2021	ANL CSE	SC LFP + ALD Al ₂ O ₃ cathode	Mar. 2022	ANL APS
SS LFP cathode	Dec. 2021	ANL CSE	SC LFP + ALD Al ₂ O ₃ cathode	Mar. 2022	ANL APS
SC LFP cathode	Dec. 2021	Northwestern University	SC LFP + ALD Al ₂ O ₃ cathode	Mar. 2022	ANL APS
SC NMC9622 cathode	Jan. 2022	Hunt Energy	SC NMC9622 + 0.25 Al cathode	Mar. 2022	ANL APS
SC LFP + C cathode	Feb. 2022	Hunt Energy	SC NMC9622 + 0.35 Al cathode	Mar. 2022	ANL APS
SS LFP cathode	Feb. 2022	Hunt Energy	SC NMC9622 + 0.45 Al cathode	Mar. 2022	ANL APS
PC NMC9622 cathode	Feb. 2022	Hunt Energy	SC LFP cathode	Apr. 2022	ANL AND
SC LFP + C cathode	Feb. 2022	ANL CAMP	SC NMC9622 cathode	Apr. 2022	ANL AND
SS LFP cathode	Feb. 2022	ANL CAMP	SC NMC9622 + 0.45 Al cathode	Apr. 2022	ANL AND

* Open to working with any group developing advanced active materials that will be beneficial for the VTO program. (Contact: yshin@anl.gov)

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Acknowledgements and Contributors

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